How to design more efficient organic dyes for dye-sensitized solar cells? Adding more sp^2-hybridized nitrogen in the triphenylamine donor

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HIGHLIGHTS

► Molecular design of dyes was done by adding NH groups in the triphenylamine donor.
► Developed dyes show significantly red-shifted maximum absorbance and longer lifetime of the first excited state.
► The changes of properties are considerably dependent on the number of the added nitrogens.

GRAPHICAL ABSTRACT
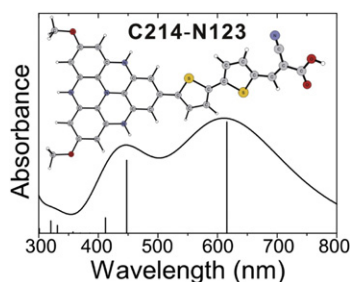
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ABSTRACT

One of the most significant aspects in the development of dye-sensitized solar cells (DSCs) is the exploration and design of high-efficiency and low-cost dyes. In the present paper, we have reported a theoretical design of potential high-efficiency organic dyes with modified triphenylamine donors, using time-dependent density functional theory with the CAM-B3LYP method. The CAM-B3LYP method is first validated to have very good performance in the descriptions of spectral properties of **C214** and **C216** dyes. With **C214** as a prototype, molecular modifications are then made and a scheme, using NH groups to connect neighboring phenyls in the triphenylamine donor, has been demonstrated to be successful to significantly red-shift the absorption maximum wavelength, extend the lifetime of the first excited state, and decrease the energy gap between HOMO and LUMO. In particular, the change amounts of these properties are illustrated to be dependent on the number of the added nitrogens, a significant finding that may perhaps make it possible to quantificationally regulate properties of organic sensitizers to match diverse requirements in the building of a high-efficiency DSC. The complementary nitrogens have been characterized to be sp^2-hybridized and shown to play an important role in assisting in charge transfer.

1. Introduction

Dye-sensitized solar cell (DSC), mainly composed of a redox electrolyte and a wide bandgap semiconductor film (particularly TiO$_2$) grafted with a quasi-monolayer of light-harvesting dye molecules, has been demonstrated to be a cost-effective photovoltaic technology and became a promising, and active, area of research [1–3]. To achieve higher efficiency of DSC, a large number of efforts have been devoted to the improvements of various processes in this complex system, among which the exploration and design of high-efficiency and low-cost dyes is always one of the most significant aspects [4–10]. At the present, metal-containing sensitizers have shown the highest performances. For example, the **N3** and **N719** sensitizers, including ruthenium polypyridyl as the framework, have attained solar energy-to-electricity conversion efficiencies of over 11% [11,12].

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Quite recently, a new record of a 12.3% efficiency was reached using a zinc-porphyrin dye (designated **YD2-o-C8**) cosensitized with **Y123** dye [13]. Besides this, metal-free organic dyes have also received growing research interest in recent years due to their high molar extinction coefficients, easily tunable optical properties, cheaper preparation processes, low toxicities, and in particular a negligible variation of photocurrents [14–23]. Several organic sensitizers, such as D149 and C217, also show very high performance with efficiencies close to 10% [24–26].

A typical organic dye consists of an electron-donor moiety, a π-conjugated bridge, and an electron-acceptor moiety, i.e. a dipolar D-π-A structure. A large number of D-π-A sensitizers have been reported with diverse types of donors, π-linkers, and acceptors. Some widely used donor groups are coumarins [27–30], carbazoles [31], N,N-dimethylaniline [32], pyrrolidine [33], tetrahydroquinolines [34], diphenylamine [35], triphenylamine [36–41], and so on. Triphenylamine and its derivatives with alkyloxy substituents have been verified to be good donors and successfully applied to the construction of many high-efficiency organic sensitizers along with different π-linkers [36–41]. This makes triphenylamine to be an excellent donor prototype to be utilized in the exploration and design of potential high-efficiency organic dyes.

Advancements in quantum chemical methods, in particular the development of density functional theory (DFT) and time-dependent DFT (TDDFT), coupled with the nearly exponential growth of computer power, have opened the door for evaluating and designing inorganic and organic sensitizers with a reasonable level of accuracy [12,42–48]. In the present work, the performance of TDDFT method with the long-range corrected CAM-B3LYP functional [49] was further validated by calculating the spectral properties of a series of organic D-π-A dyes with the triphenyl-amine donor. The computational results reveal very good performance of CAM-B3LYP and the best matching with experiments in the cases of **C214** and **C216**. With **C214** as a prototype, molecular modifications were then made in order to design potential high-efficiency sensitizers and a scheme, using NH groups to connect neighboring phenyls in the triphenylamine donor, has been demonstrated to be successful to significantly red-shift the absorption maximum wavelength, extend the lifetime of the first excited state, and decrease the energy gap between HOMO and LUMO. Interestingly, the change amounts of these properties were found to be dependent on the number of the added nitrogens. The complementary nitrogens have been characterized to have a sp²-hybridized character and their effects have been discussed in detail. Based on these calculations, some potential excellent organic dyes have finally been recommended in this paper.

2. Computational methods

All calculations were implemented in the Gaussian 09 package [50]. The ground-state geometries of all organic dyes were optimized using density functional theory (DFT) with the hybrid functional B3LYP [51–53], coupled with the 6-31 + G(d,p) basis set. Solvation effects were included during the optimizations using a polarizable continuum model according to the CPCM method [54–57]. The chloroform solvent was employed throughout this investigation. Frequency calculations were performed at the same level of theory as the optimizations to confirm the nature of the minima. Based on the optimized ground-state geometries, the UV–vis spectra of dyes were obtained by performing single-point time-dependent DFT (TDDFT) calculations with the long-range corrected CAM-B3LYP functional [49] and 6-31 + G(d,p) basis set, with solvation effects included also.

The lifetime of the excited state (τ) is an important factor for considering the efficiency of charge transfer of organic dyes. A dye with a longer lifetime in the excited state is expected to be more facile for charge transfer. In the present investigation, the τ value was approximately set to the lifetime of spontaneous luminescence, which is estimated by [58]

$$\tau = \frac{1}{A_{k,k'}}, \quad A_{k,k'} = \frac{4e^2 \Delta E_{k',k}^3}{3\hbar^4 c^3} |r_{k,k'}|^2 \qquad (1)$$

where $A_{k,k'}$ is Einstein coefficient for spontaneous emission, e is the elementary charge, $\hbar$ is the reduced Planck's constant, and c is the speed of light in vacuum. Moreover, $\Delta E_{k',k}$ and $r_{k,k'}$ represent the transition energy and transition dipole moment from states k to k', respectively.

3. Results and discussion

3.1. Further validation of method for organic dyes with the triphenylamine donor

The development of TDDFT has made it possible to calculate UV–vis absorption spectra of dyes at a reasonable level of accuracy. Although the computed vertical excitation energies (the energy difference between the excited states and the optimized ground state without zero-point vibrational corrections) do not have an actual experimental correspondence, the application of a proper DFT functional to a certain series of dyes may reproduce the experimental electronic absorption properties, in particular absorption maximum wavelength (λ_{max}), which is usually corresponding to the calculated excitation energy (ΔE) for the lowest excited state. Using a well-assessed functional, the comparison of TDDFT results among related dyes should promote the understanding of the known efficiencies and also be able to give a reliable prediction of the efficiency of a designed dye. The long-range corrected CAM-B3LYP functional [49] has been reported to be an accurate method for the computations of typical organic D-π-A dyes with the triphenylamine donor, such as L0, L4, D5, C217, and so on [47,48]. In the present work, its performance was further examined by applying it to six organic dyes with different conjugated linkers such as furan, bifuran, thiophene, bithiophene, selenophene, and biselenophene, i.e. the **C209**, **C210**, **C213**, **C214**, **C215**, and **C216** dye sensitizers (see Fig. 1). Its capability in the descriptions of π-linkers with different sizes and heteroatoms has been evaluated in these calculations. To reduce computational consumptions, all hexyloxy substituents in these dyes were replaced by methoxyls. The chloroform solvent was used for all investigated dyes.
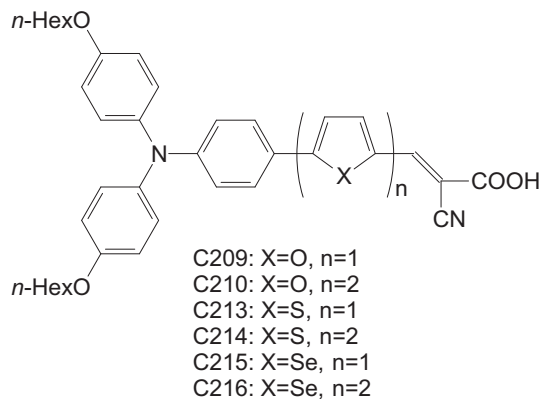

Fig. 1. Molecular structures of the **C209**, **C210**, **C213**, **C214**, **C215**, and **C216** dye sensitizers.

All ground-state geometries of dyes were optimized at the B3LYP/6-31 + G(d,p) theory level with the CPCM polarizable continuum model employed [54–57]. As a representative, optimized structure and frontier orbitals of **C214** are given in Fig. 2. As expected, in **C214**, the π-linker and acceptor moieties are almost at a plane, as well as the nitrogen atom (N1) in the triphenylamine donor. Furthermore, the three N1-connected carbons at the phenyls are also placed at the same plane (see Fig. 2), indicating that the N1 lone pair participates in the π-conjugated system and the sp^3-hybridized N1 atom turns to a sp^2-hybridized character. However, the two terminal alkyloxy-substituted phenyls are rotated along the σ N−C bonds due to the congested steric effects between phenyls and thus out of the plane described above. The dihedral angles composed of two adjacent phenyls are −52.8, −52.0, and 128.4°, respectively (Fig. 2). This geometrical characteristic may introduce a conjecture, that is, if the improvement of molecular planarity, especially in the triphenylamine donor moiety, is able to increase the efficiencies of this type of dyes. This will be discussed in detail in the next section. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of **C214** show π and π* character, respectively. The HOMO is delocalized almost over the whole molecule and slightly more localized at the donor moiety. The LUMO presents the same large delocalization but a little more localization at the acceptor. This is expected to facilitate the charge separation of the dye sensitizer upon photoexcitation. The energies of the **C214** HOMO and LUMO are calculated to be −5.12 and −3.09 eV, respectively, and consequently the energy gap between them (ΔE_{HL}) is 2.03 eV (entry 4 in Table 1). It is satisfying to find that the LUMO of **C214** lies in energy above the conduction band minimum of the isolated TiO$_2$ (−3.24 eV) [45] and the HOMO is placed within the bandgap of TiO$_2$ (see entries 4 and 7 in Table 1), a crucial characteristic that confirms the feasibility of **C214** as a sensitizer for DSC. Other studied organic dyes (**C209**, **C210**, **C213**, **C215**, and **C216**) are computed to have the same geometrical and orbital properties as those of **C214**. An additional finding is that the ΔE_{HL} value is decreased with the elongation of the π-conjugated linker and/or the increase of atomic number of the heteroatom (entries 1−6 in Table 1). For example, with the same heteroatom in the π-linker, the ΔE_{HL} follows the orders: **C209** (2.42 eV) > **C210** (2.12 eV), **C213** (2.33 eV) > **C214** (2.03 eV), and **C215** (2.30 eV) > **C216** (1.97 eV), while the arrays of **C209** > **C213** > **C215** and **C210** > **C214** > **C216** are observed with the same number of five-membered aromatic heterocycle in the π-linker.

Using the TDDFT method with the CAM-B3LYP functional, the calculations of electronic absorption spectra gave absorption maxima (λ_{max}) for these dyes (see Table 1), which follow the reverse pattern relative to the ΔE_{HL} values, that is, the orders of **C209** (482 nm) < **C210** (504 nm), **C213** (485 nm) < **C214** (518 nm), and **C215** (500 nm) < **C216** (553 nm) and/or the orders of **C209** < **C213** < **C215** and **C210** < **C214** < **C216**. This indicates that the increase in the length of π-conjugated linker moiety and the use of heavier heteroatom in π-linker both lead to red shift in
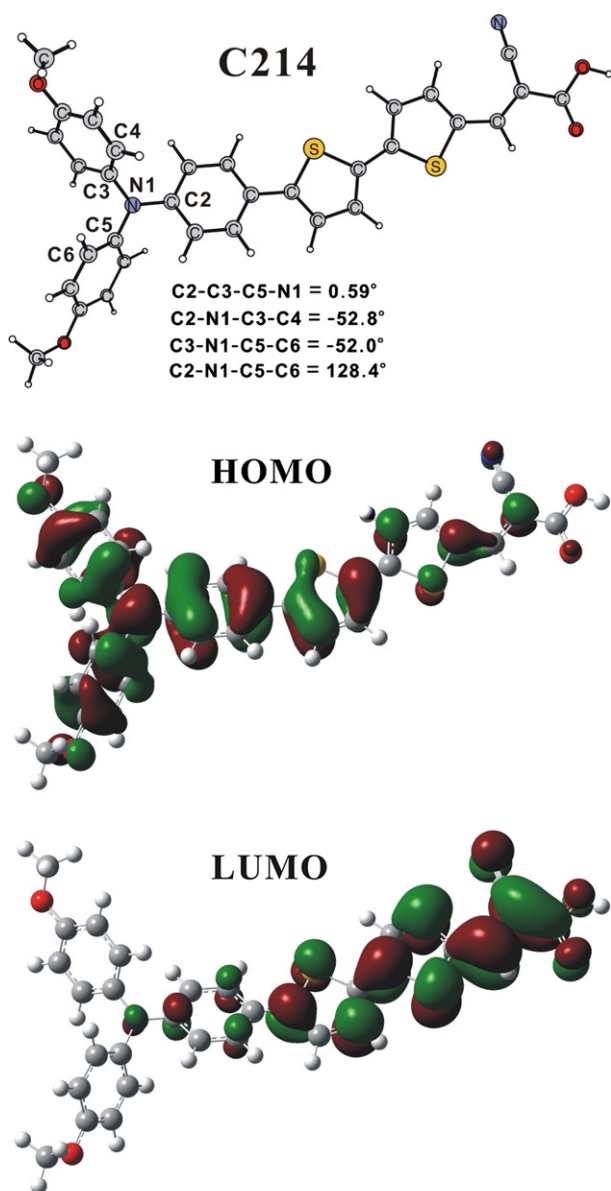

Fig. 2. Optimized structure of the **C214** dye in chloroform and its HOMO and LUMO. The key dihedral angles are shown in degree.

Table 1
Calculated properties of organic dyes in chloroform.[a]

Entry	Dye	Exp. λ_{max}[b] (nm)	Cal. λ_{max}[c] (nm)	ΔE_L[d] (eV)	f_L[e]	E_H[f] (eV)	E_L[g] (eV)	ΔE_{HL}[h] (eV)	μ[i] (D)
1	**C209**	506	482	2.57	1.246	−5.24	−2.82	2.42	10.07
2	**C210**	522	504	2.46	1.752	−5.09	−2.97	2.12	13.02
3	**C213**	514	485	2.56	1.438	−5.25	−2.92	2.33	11.40
4	**C214**	523	518	2.39	1.806	−5.12	−3.09	2.03	12.93
5	**C215**	525	500	2.48	1.487	−5.26	−2.96	2.30	12.16
6	**C216**	549	553	2.24	1.816	−5.14	−3.17	1.97	14.13
7	TiO$_2$[j]	−	−	3.65	−	−7.70	−3.24	4.46	−
8	**C214−C123**	−	517	2.40	1.727	−4.98	−3.11	1.88	14.42
9	**C214−O123**	−	504	2.46	1.633	−4.98	−3.15	1.83	11.91
10	**C214−N123**	−	616	2.01	1.013	−4.30	−3.08	1.22	15.44
11	**C214−N1**	−	558	2.22	1.550	−4.59	−3.08	1.51	16.32
12	**C214−N2**	−	558	2.22	1.379	−4.61	−3.10	1.51	14.81
13	**C214−N12**	−	610	2.03	1.270	−4.39	−3.07	1.32	16.31
14	**C214−N23**	−	593	2.09	1.035	−4.40	−3.10	1.29	14.35

[a] All properties were calculated at the CAM-B3LYP/6-31 + G(d,p) level.
[b] Experimental absorption maximum wavelength from ref. [41].
[c] Calculated absorption maximum wavelength.
[d] Calculated excitation energy for the lowest excited state, which is corresponding to cal. λ_{max}.
[e] Oscillator strength for the lowest excitation.
[f] The energy of the highest occupied molecular orbital (HOMO).
[g] The energy of the lowest unoccupied molecular orbital (LUMO).
[h] Energy gap between HOMO and LUMO.
[i] Molecular dipole moment in debye (D).
[j] Values for the isolated TiO$_2$ are obtained from ref. [45].

absorption spectra. This finding is consistent with the experiments [41]. It is further observed that the CAM-B3LYP-computed λ_{max} of **C214** (518 nm) and **C216** (553 nm) shows the best agreement with the experimental values (523 and 549 nm, respectively, entries 4 and 6 in Table 1) [41]. For other dyes, the CAM-B3LYP calculations underestimate the λ_{max} (Table 1), i.e. overestimate the excitation energy for the lowest excited state (ΔE_L). This can be rationalized by considering the deficiency of exchange-correlation functionals in the description of the excitation involving charge separation, that is, the absence of the accurate $1/R$-dependence (R is the distance of charge separation) in most of functionals. The inclusion of the exact exchange interaction in hybrid functionals such as B3LYP and PBE0 can partially reduce this insufficiency. However, it is often not perfect since the introduced dependence is not $1/R$ usually. For example, the B3LYP functional involves a dependence of $0.2/R$. As a result, the excitation energy for the charge transfer interaction trends to be underestimated with the increase of the distance between the charge donor and acceptor. In the present cases, the ΔE_L overestimations for the dyes with only one heterocycle in linkers (**C209**, **C213**, and **C215**) are to a certain extent canceled with one more heterocycle added in the conjugated systems (i.e. for **C210**, **C214**, and **C216**) and the best balance is achieved in the cases of **C214** and **C216** (see Table 1). The similar effects were also observed in the theoretical studies of the **NKX-2553**, **NKX-2554**, and **NKX-2569** dyes, where the last one has a longer π-conjugated linker than the other two and shows an underestimation of the excitation energy for the first excited state [45]. In general, the TDDFT method with the CAM-B3LYP functional performs well in the descriptions of electronic absorption spectra of these dyes, particularly successfully in the prediction of ΔE_L for **C214** and **C216**. This makes it possible to use **C214** and/or **C216** as an appropriate molecular prototype in the design of potential high-efficiency sensitizers, coupled with the utilization of the CAM-B3LYP functional.

3.2. Molecular modifications of C214

The exploration and design of more efficient dyes are of significance for the development of DSC. As discussed above, the **C214** and **C216** dyes are suitable molecular templates for geometrical alterations in order to find potential excellent dyes. In the present investigation, considering the difficulties and consumptions in the future syntheses, the **C214** dye instead of **C216** was chosen as the prototype for the subsequent design of new organic sensitizers. There are two tactics for molecular modifications of **C214**. One is to improve the planarity of the tri-phenylamine donor moiety. As pointed out above, the alkyloxy-substituted phenyls in **C214** are not placed at the plane of the π-linker and acceptor moieties due to congested steric problems. The perfection of the donor planarity is supposed to enhance the π-conjugated effect of the entire molecule and consequently improve the performance of organic dye as a sensitizer. Another scheme of modification derives from the fact that the sp^2-hybridized nitrogen in the triphenylamine donor is the main electron contributor in charge transfer. This can be confirmed by an optimization of the **C214** cation radical, i.e. the product after charge transfer, where the nitrogen has the largest unpaired spin density population (0.24) compared to other atoms (Fig. 3). Therefore, the second proposal for the modification of **C214** is to add more nitrogen to the donor moiety. To account for these two schemes of modification, we used various small groups to connect the neighboring phenyls at their *ortho*-positions (see Fig. 4). When the connecting groups were sp^3-hybridized methylenes (CH_2), the resulting **C214** derivative (denoted by **C214–C123**) was expected to have an excellent molecular planarity and thus be able to satisfy the first
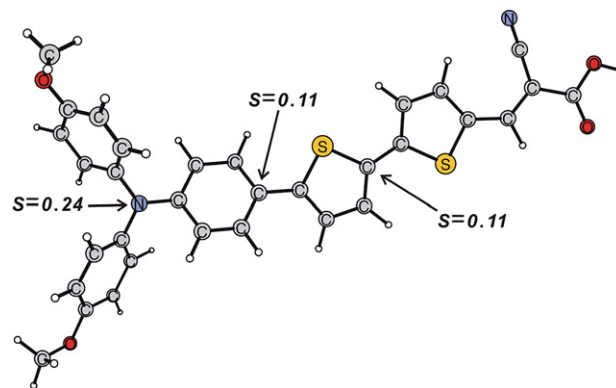

Fig. 3. Optimized structure of the **C214** cation radical in gas phase. The major unpaired spin density populations are shown.

modification tactics. Furthermore, the **C214** derivative (referred to as **C214–N123**) resulting from the use of secondary amines (NH) would account for both of modification schemes. As a test, oxygen atoms were also employed as connecting species and the corresponding derivative was named by **C214–O123**.

As supposed, all optimized **C214** derivatives present very good planarity in geometry (their optimized geometries are given in the Supplementary data). In particular, the three phenyls are now lay on the plane composed of the π-linker and acceptor moieties. However, unfortunately, the **C214–C123** derivative does not show big differences in electronic absorption spectrum from the original **C214** dye (see Fig. 5). For example, **C214–C123** has only one absorption peak in the visible-light range, just like **C214**, and its absorption maximum wavelength (λ_{max} = 517 nm, entry 8 in Table 1) is only 1 nm smaller than that of **C214** (518 nm, entry 4 in Table 1). This demonstrates that the improvement of the planarity of the triphenylamine donor would not change the performance of organic dyes considerably. Moreover, the use of oxygen atoms as the connecting groups (i.e. **C214–O123**) even shifts the absorption peak toward the blue part of the spectrum (λ_{max} = 504 nm, entry 9 in Table 1), which is probably attributed to the strong electronegativity of oxygen.

In contrary to **C214–C123** and **C214–O123**, the alteration of **C214** using amines (i.e. **C214–N123**) gave very exhilarating results. The λ_{max} of **C214–N123** is significantly red-shifted to 616 nm (entry 10 in Table 1), almost 100 nm larger than that of **C214**. Besides the
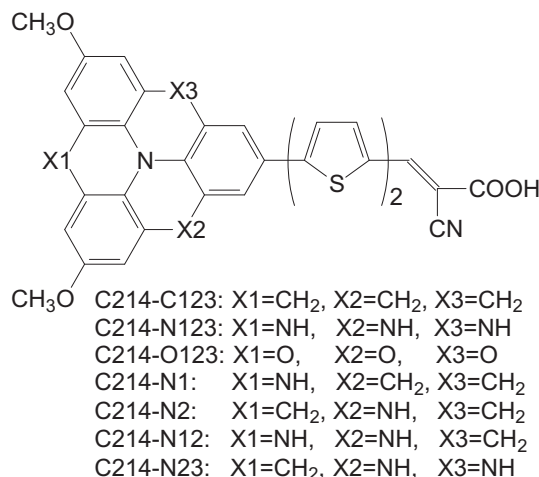

Fig. 4. Molecular structures of the **C214** derivatives designed in the present work.
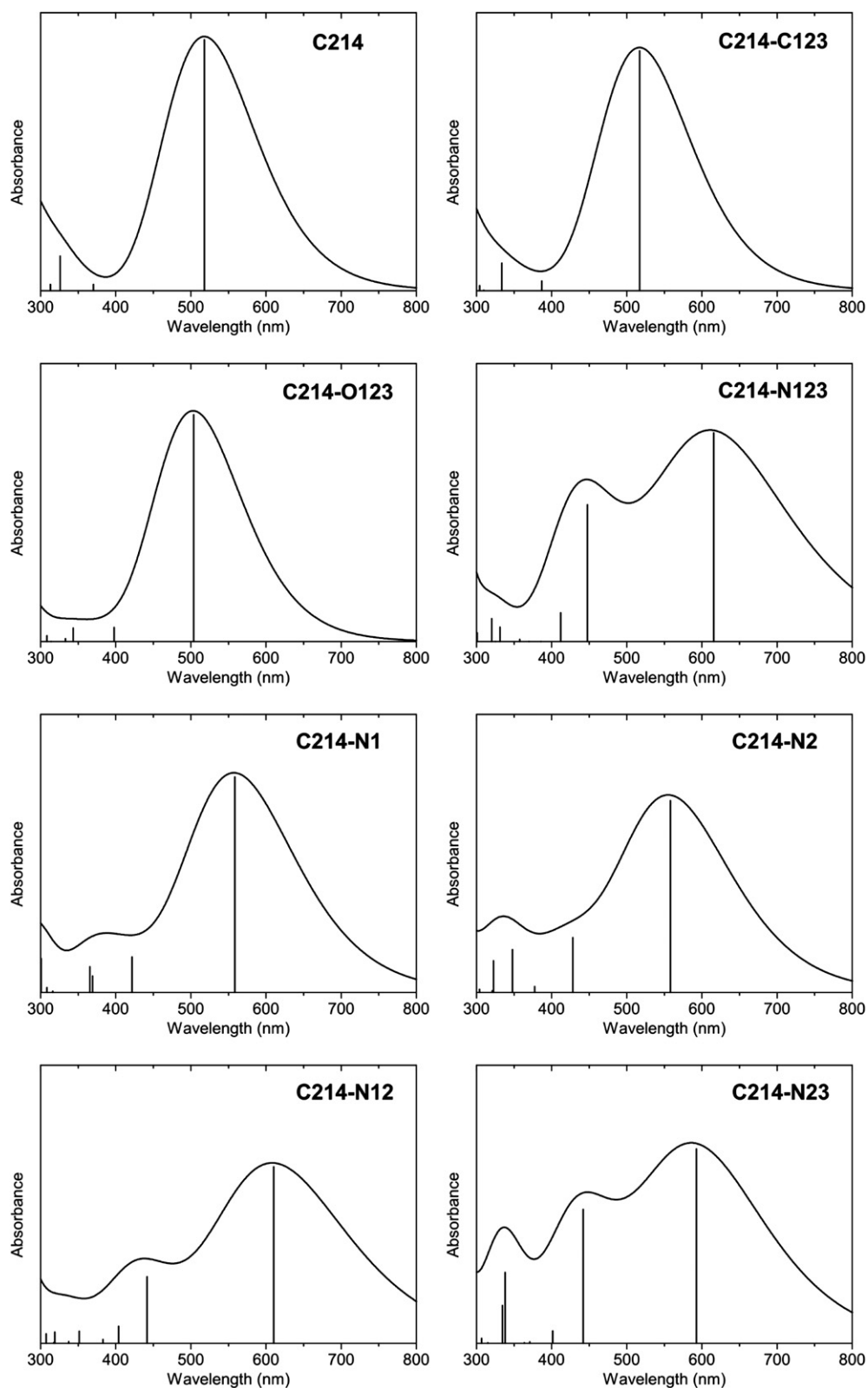
Fig. 5. Electronic absorption spectra of **C214** and its derivatives dissolved in chloroform.

Table 2
Lifetimes for the first excited states (τ) of **C214** and its derivatives in chloroform.[a]

Entry	Molecule	ΔE_L (eV)[b]	f_L[c]	$r_{k',k}$[d]	τ ($\times 10^{-9}$ s)[e]	Wave function (coefficient)[f]
1	**C214**	2.39	1.806	30.789	2.2	H → L (0.56), H − 1 → L (−0.38), H → L + 1 (0.14)
2	**C214−N123**	2.01	1.013	20.533	5.6	H → L (0.61), H − 1 → L (0.12), H − 3 → L (−0.20), H → L + (0.23)
3	**C214−N1**	2.22	1.550	28.506	3.0	H → L (0.56), H − 1 → L (0.35), H → L + 1 (0.18)
4	**C214−N2**	2.22	1.379	25.346	3.4	H → L (0.59), H − 1 → L (0.31), H → L + 1 (0.19)
5	**C214−N12**	2.03	1.270	25.523	4.4	H → L (0.61), H − 1 → L (−0.15), H − 2 → L (0.22), H → L + 1 (0.21)
6	**C214−N23**	2.09	1.035	20.189	5.1	H → L (0.61), H − 2 → L (0.25), H → L + 1 (0.22)

[a] All properties were calculated at the CAM-B3LYP/6-31 + G(d,p) level.
[b] Calculated excitation energy for the first excited state.
[c] Oscillator strength.
[d] Transition dipole moment.
[e] Lifetime for the first excited state.
[f] H and L signify HOMO and LUMO, respectively.

excitation peak at λ_{max}, **C214−N123** has two additional excitations at 448 nm and 412 nm (see Fig. 5) with oscillator strengths of 0.665 and 0.140, respectively. These two excitations greatly broaden the absorption range of **C214−N123** and expand it over the whole visible-light range. This gives an indication that **C214−N123** is probably an excellent broad-spectrum organic dye. Furthermore, the addition of nitrogens to the donor terminal also notably raises molecular dipole moment to 15.44 D (entry 10 in Table 1), from a value of 12.93 D in **C214** (entry 4 in Table 1). The increased dipole moment may facilitate the charge separation of **C214−N123** upon photoexcitation. Hence, the evidences described here finally give an exciting hint that the **C214−N123** derivative is most likely a potential broad-spectrum and high-efficiency sensitizer for dye-sensitized solar cell.

The further characterization of **C214−N123** was made by scrutinizing into its orbital properties. The energy gap between HOMO and LUMO in **C214−N123** (ΔE_{HL} = 1.22 eV, entry 10 in Table 1) is much smaller than that of **C214** (2.03 eV, entry 4 in Table 1). This is mainly attributed to the remarkable raise of the HOMO energy, while the energy of LUMO (−3.08 eV) is hardly changed and still situated above the conduction band minimum of the isolated TiO$_2$ (−3.24 eV, entry 7 in Table 1). The excitation analysis demonstrates that the transition from HOMO to LUMO is the main contribution to the lowest electronic excitation, although the transitions from other occupied orbitals (such as HOMO − 1) also make contributions (see entry 2 in Table 2). For further investigations, the key orbitals of **C214−N123** are displayed in Fig. 6. It can be seen from Fig. 6 that all nitrogens in the donor take part in the construction of HOMO but less in that of LUMO. A molecular orbital analysis shows that it is p$_z$ orbitals of nitrogens that essentially participate in HOMO and therefore all donor nitrogens also have sp^2-hybridized character. This points out that all nitrogens in the donor of **C214−N123** may assist in or directly contribute to the charge separation, using their lone pairs. Although a subsequent optimization of the **C214−N123** cation radical (see Fig. 7) reveals only small unpaired spin density populations at the added nitrogens (with amounts of ∼0.1), the original nitrogen in the center of the donor moiety is shown to have a higher spin density (0.30) than that of the **C214** cation radical (0.24, Fig. 3), thereby confirming the role of the added nitrogens in assisting in the charge transfer and the dominant donation of the original nitrogen in the charge-transfer process.

Using formula (1), a further calculation shows that the first excited state of **C214−N123** has a longer lifetime (τ = 5.6 × 10^{-9} s, entry 2 in Table 2) than that of **C214** (2.2 × 10^{-9} s, entry 1 in Table 2), implying that, when devised in DSC, **C214−N123** is more likely a good sensitizer for charge transfer instead of an efficient fluorescent agent. The achievement of the longer lifetime in the excited state should attribute to the decrease of both the excitation energy

and transition dipole moment when additional nitrogens are brought in (Table 2). With all results discussed here, it can be concluded that the addition of three nitrogens in the triphenylamine donor almost certainly creates a potential good organic sensitizer for DSC, i.e. the **C214−N123** derivative. Of course, to exert the latent ability of **C214−N123**, it is necessary to incorporate a suitable redox electrolyte.

Now that the introducing of nitrogens to the triphenylamine donor is an effective approach to develop organic sensitizers, an interesting topic is emerging, that is, how about the effects of the number and positions of the supplementary nitrogens. To assess them, we prepared other four **C214** derivatives with one and two NH groups added in the donor moiety, respectively (see Fig. 4). **C214−N1** and **C214−N2** are the one-NH-added molecules with the NH group at positions X1 and X2, respectively. The other two positions are filled in using the CH$_2$ groups since it has been demonstrated above that the use of methylenes (i.e. **C214−C123**) hardly changes any spectral properties. As positions X2 and X3 are almost equivalent, it is unnecessary to build a molecule with a NH at the position of X3. The same pattern was followed in the assembly of **C214−N12** and **C214−N23**, which are the molecules with two NH at positions (X1,X2) and (X2,X3), respectively. The calculations of these modified molecules reveal an important rule, that is, the main spectral properties of this type of dyes are to a great extent dependent on the number of the added nitrogens. For example, their λ_{max} values (Table 1) are calculated to be 518 nm (**C214**) << 558 nm (**C214−N1**) = 558 nm (**C214−N2**) << 593 nm (**C214−N23**) < 610 nm (**C214−N12**) < 616 nm (**C214−N123**). This means that the addition of more nitrogen is able to reach larger red shift in absorption spectra. Meanwhile, the employment of more nitrogen in the donor moiety is capable of extending the lifetime of the first excited state (τ) more significantly (Table 2). The τ values of **C214** and its derivatives with NH groups included are predicted to be 2.2 × 10^{-9} s (**C214**) < 3.0 × 10^{-9} s (**C214−N1**) < 3.4 × 10^{-9} s (**C214−N2**) < 4.4 × 10^{-9} s (**C214−N12**) < 5.1 × 10^{-9} s (**C214−N23**) < 5.6 × 10^{-9} s (**C214−N123**). Also, the energy height of HOMO is raised more considerably with more nitrogen included which subsequently results in smaller energy gap between HOMO and LUMO (Table 1), i.e. 2.03 eV (**C214**) > 1.51 eV (**C214−N1**) = 1.51 eV (**C214−N2**) > 1.32 eV (**C214−N12**) ≈ 1.29 eV (**C214−N23**) > 1.22 eV (**C214−N123**). Another finding in the computations of these molecules is that the position for the added nitrogen has less effect on most of properties, but poses a noticeable influence on molecular dipole moment. It can be seen that the addition of nitrogen at the terminal position X1 can lead to bigger dipole moment (Table 1). For instance, **C214−N1**, the molecule with only one NH group at the position of X1, has the biggest dipole moment (16.32 D, entry 11 in Table 1) compared to other molecules computed in the present paper. In summary, the results here
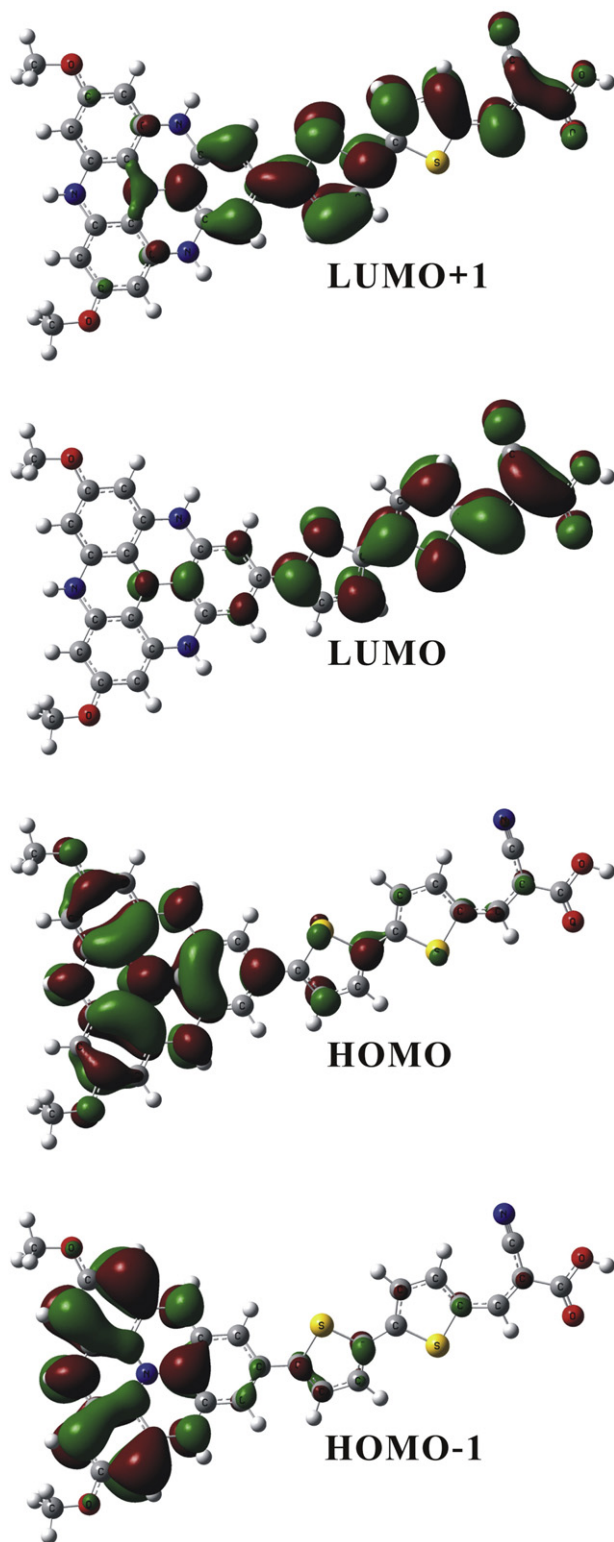
Fig. 6. Key orbitals involved in photoexcitation for the **C214**–**N123** molecule.
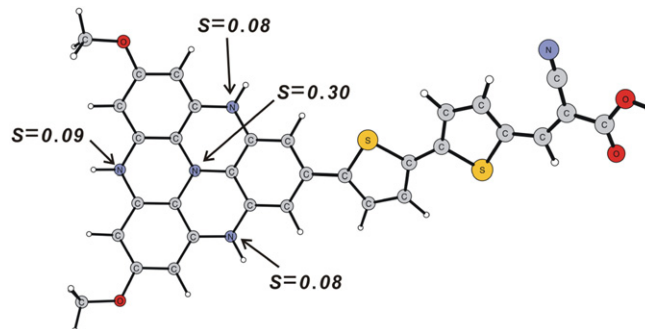
Fig. 7. Optimized structure of the **C214**–**C123** cation radical in gas phase, along with the major unpaired spin density populations.

4. Conclusions

In this paper, we have reported a theoretical design of potential high-efficiency organic dyes for dye-sensitized solar cells (DSCs), using time-dependent density functional theory (TDDFT) with the CAM-B3LYP method. The CAM-B3LYP method has first been validated to have very good performance in the descriptions of the spectral properties of a series of organic D-π-A dyes with the triphenylamine donor, especially in the cases of the **C214** and **C216** dyes. With **C214** as a prototype for molecular modifications, a scheme by using NH groups to connect adjacent phenyls in the triphenylamine donor of **C214** (see structures in Fig. 4) was indicated to be able to considerably red-shift the absorption maximum wavelength ($\lambda_{\max}$), extend the lifetime of the first excited state, and decrease the energy gap between HOMO and LUMO. In particular, it has been demonstrated that the change amounts of these properties are dependent on the number of the added nitrogens, a feature that is of significance since it may make it possible to quantificationally adjust the properties of organic sensitizers to match various requirements in the building of a high-efficiency DSC. The further fine regulation can be made by the selection of positions of additional nitrogens, which has less effect on most of dye properties but exerts an apparent influence on molecular dipole moment. The introduced nitrogens have been illustrated to participate in the construction of HOMO with a sp^2-hybridized character, and play an important role in assisting in charge transfer. On the basis of these results, a series of potential good organic dyes derived from **C214** by adding one or more NH groups to the triphenylamine donor (see Fig. 4) can be suggested here to be utilized in the assembly of high-efficiency DSC. To further gain better rectification for these **C214** derivatives, a possible way is to replace the hydrogens in the NH groups by long-chain alkyls. In addition, it is worth mentioned here that the improvement of the triphenylamine planarity, originated from the connections between neighboring phenyls, hardly affects spectral properties of organic dyes. Finally, the effects of the sp^2-hybridized nitrogen summarized here should also be effective for different kinds of donors and thus very useful for the development of other DSC dyes.

indicate the dependence of organic dye properties on the number (and partially the positions) of nitrogens added in the triphenylamine donor, which may be a useful tool utilized to regulate the properties of organic sensitizers in order to devise a high-efficiency DSC.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jpowsour.2012.09.053.

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